



Photocatalytic reduction of nitrate ions to dinitrogen over layered perovskite $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ using water as an electron donor

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ABSTRACT

Photocatalytic reduction of NO_3^- to produce NO_2^- , NH_4^+ , and N_2 proceeded on $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ powder under UV irradiation accompanied with photochemical decomposition of NO_3^- to NO_2^- and O_2 without any sacrificial reagents. Loading of Cu and Ni cocatalysts enhanced the photocatalytic reaction to form N_2 . Ni was the most effective cocatalyst. The $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ photocatalyst with the Ni cocatalyst loaded by an impregnation method and subsequent H_2 reduction showed high activity for the reduction of NO_3^- to form NO_2^- , NH_4^+ , and N_2 . O_2 also formed as an oxidation product of water. The ratio of the number of reacted electron to that of hole was almost unity, indicating water was consumed as an electron donor for the reduction of NO_3^- . A boric acid of a buffer for pH control was effective to obtain a high yield of N_2 . The N_2 yield reached 85% in the presence of a boric acid after 10 h using a 400 W high-pressure mercury lamp in 10 mmol/L of an aqueous NaNO_3 solution, while it was 50% without the boric acid. The N_2 yield was almost 100% when 3 mmol/L of an aqueous NaNO_3 solution was used with a boric acid.

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1. Introduction

Nitrate ions contained in agricultural and industrial wasted water cause water pollution. Therefore, the development of efficient and clean processes for the elimination of nitrate ions has attracted attention. Electrochemical [1], photocatalytic [2–25], and biological [26] methods have been reported as the candidates for the process as well as a physical separation using a semipermeable membrane [27]. Among them, the photocatalytic process is very simple because just the dispersion of photocatalyst powder can be used: that is the significant advantage for the photocatalytic process. TiO_2 [2–18], ZnO [19], $\text{H}_4\text{Nb}_6\text{O}_{17}$ [6], SrTiO_3 [2,4], $\text{K}_x\text{Ga}_x\text{Sn}_{8-x}\text{O}_{16}$ [20], tantalates [21], CdS [22–24], and Ni-doped ZnS [25] have been reported as photocatalysts for reduction of nitrate ions. ZnO [19] with a wide band gap and CdS [2,22,23] with a visible light response are active photocatalysts for the reduction of nitrate ions to nitrite ions in the presence of reducing reagents

such as methanol without any cocatalysts. TiO_2 , SrTiO_3 , and CdS photocatalysts can produce NH_3 from NO_2^- [2]. Cocatalyst and reaction condition are important for the activity and selectivity of photocatalytic reduction of nitrate ions as for water splitting. For example, when Cu/TiO_2 is used, NH_3 and NO_2^- are obtained in acidic and basic aqueous solutions, respectively [8]. TiO_2 photocatalyst loaded with Cu–Pd alloy cocatalyst gives NH_3 efficiently [13]. Photocatalysts that can reduce NO_3^- to N_2 of a harmless product in the presence of sacrificial reagents are TiO_2 co-loaded with Pd and Cu [8], $\text{TiO}_2\text{:W,N}$ [14], $\text{H}_4\text{Nb}_6\text{O}_{17}$ [6], and $\text{K}_x\text{Ga}_x\text{Sn}_{8-x}\text{O}_{16}$ [20] with UV light responses, and ZnS:Ni [25] with visible light response. However, a clean process should not require any sacrificial reagents. Noble metal cocatalyst-loaded TiO_2 [3–5] and Ni cocatalyst-loaded tantalate [21] photocatalysts reduce NO_3^- in the absence of sacrificial reagents accompanied with O_2 evolution of an oxidation product of water. Among them, Ni-loaded KTaO_3 photocatalyst shows high activity that 44% of NO_3^- can be converted to N_2 after 25 h using a 400 W high pressure mercury lamp [21]. We found that NiO-loaded $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ photocatalyst with layered perovskite structure shows high activity for water splitting into H_2 and O_2 in a stoichiometric amount [28]. The $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ photocatalyst powder with a plate-like shape reflecting the layered perovskite structure can be prepared by a polymerizable complex method. When Ag cocatalyst is loaded on the $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ powder, the photocatalyst is active for CO_2 reduction into CO using water

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Table 1
NO₃[−] reduction over BaLa₄Ti₄O₁₅ photocatalyst with various cocatalysts.

Cocatalyst (wt%) ^a	Amounts of products after 10 h/μmol					Selectivity ^b %	N ₂ yield ^c %	e [−] /h ⁺
	Reduction product				Oxidation product O ₂			
	H ₂	N ₂	NO ₂ [−]	NH ₄ ⁺				
None	0.3	13	1900	0	1300	99	0.7	0.8
Ni(0.5)	5200	800	210	700	8300	57	45	0.7
Ni(1.0)	3100	790	320	610	7000	68	45	0.7
Ni(2.0)	960	810	960	510	5000	88	46	0.8
Ag(1.0)	1.5	13	2700	0	1300	99	0.7	1.1
Cu(1.0)	78	140	3000	0	2100	97	8	0.9

Catalyst: 0.5 g, solution: 10 mmol L^{−1} of an aqueous NaNO₃ solution (350–370 mL), a 450 W high pressure mercury lamp, an inner irradiation quartz cell,

^a Loading method of cocatalyst: impregnation and H₂ reduction.

^b (2NO₂[−] + 8 NH₄⁺ + 10 N₂)/(2H₂ + 2NO₂[−] + 8 NH₄⁺ + 10 N₂) × 100.

^c (2N₂)/(an initial amount of NO₃[−]) × 100.

as an electron donor [29]. It is interesting to apply this excellent BaLa₄Ti₄O₁₅ photocatalyst to the reduction of NO₃[−] employing suitable cocatalysts. We preliminary reported the reduction of NO₃[−] using the BaLa₄Ti₄O₁₅ photocatalyst [30].

In the present study, photocatalytic reduction of NO₃[−] into N₂ was investigated using the BaLa₄Ti₄O₁₅ photocatalyst loaded with Ni cocatalyst that was effective for tantalate photocatalysts such as KTaO₃. Effects of a H₃BO₃ buffer on the activity and selectivity were examined. The reaction paths were also investigated.

2. Experimental

2.1. Preparation of BaLa₄Ti₄O₁₅ photocatalyst and a loading method of a cocatalyst

BaLa₄Ti₄O₁₅ photocatalyst was prepared by a polymerizable complex method according to the previously reported procedure [28,29]. BaCO₃ (Kanto chemical; 99.0%), Ti(OC₄H₉)₄ (Kanto chemical; 97.0%), La(NO₃)₃·6H₂O (Wako; 99.9%), propylene glycol (Kanto chemical; 99.0%), and citric acid (Sigma Aldrich; 99.0%) were used as starting materials. An aqueous Ni(NO₃)₂ solution containing the photocatalyst was evaporated to dryness and the resulting solid was calcined at 543 K in air. Reduction treatment was performed in the presence of 200 Torr of H₂ gas at 773 K for 2 h to obtain metallic Ni cocatalyst-loaded BaLa₄Ti₄O₁₅ photocatalyst.

2.2. Characterization

The photocatalyst was identified as a single phase by powder X-ray diffraction (Rigaku; Miniflex, Cu Kα). Scanning electron microscopy (SEM) images were taken using a JEOL JSM-6700F.

2.3. Photocatalytic reaction

Photocatalytic NO₃[−] reduction was carried out in a gas-closed circulation system using an inner irradiation quartz cell containing 350–370 mL of an aqueous NO₃[−] suspension of the photocatalyst (0.5 g). pH was controlled by an addition of H₃BO₃ into the suspension, if needed. A 400 W high-pressure mercury lamp was used as a light source. Gaseous products of H₂, O₂, and N₂ were determined by a gas chromatograph (Shimadzu, GC-8A) with a thermal conductivity detector (MS-5A, Ar carrier). NO₃[−] of a reactant, and NO₂[−] and NH₄⁺ of products were analyzed by an ion chromatograph (TOA-DKK, ICA-2000, DS-plus, columns for cations and anions: PCI-302S and PCI-230, eluents for cations and anions: 4 mmol/L of HNO₃aq. (pH 2.4) and a mixed solution of 0.8 mmol/L of Na₂CO₃aq. and 2.4 mmol/L of NaHCO₃aq. (pH 9.9)).

3. Results and discussion

3.1. Photocatalytic reduction of NO₃[−] over BaLa₄Ti₄O₁₅ photocatalyst

Table 1 shows NO₃[−] reduction over BaLa₄Ti₄O₁₅ photocatalyst with various cocatalysts. Naked BaLa₄Ti₄O₁₅ photocatalyst gave NO₂[−] and O₂. This is mainly due to not photocatalytic but photochemical reaction under UV irradiation (λ < 300 nm) [21]. A significant decrease in NO₂[−] and increases in N₂, NH₄⁺, and H₂ were observed when Ni cocatalyst was loaded by an impregnation method and subsequent H₂ reduction. The activity depended on the loading amount of the Ni cocatalyst. The maximum N₂ yield and maximum total amounts of reacted electrons and holes were obtained at 0.5 wt% of the Ni cocatalyst. N₂, NH₄⁺, and H₂ were formed by photocatalytic reactions, whereas NO₂[−] formed by not only photocatalytic but also photochemical reactions.

Ag cocatalyst did not give any significant effect on the photocatalytic NO₃[−] reduction, although NO₂[−] formation was enhanced. N₂ formation was enhanced on Cu cocatalyst-loaded BaLa₄Ti₄O₁₅ photocatalyst compared with naked BaLa₄Ti₄O₁₅. Although Cu cocatalyst gave a large amount of NO₂[−] than Ni cocatalyst, formations of N₂ and NH₄⁺ were suppressed as well as H₂ formation. The behaviors for NO₂[−] and NH₄⁺ formations on the Cu cocatalyst-loaded BaLa₄Ti₄O₁₅ photocatalyst were similar to those on Cu/TiO₂ in a basic aqueous solution [8]. These results were due to a large overpotential of Cu toward H₂ formation.

Ni cocatalyst that was loaded by an impregnation method and subsequent H₂ reduction showed high performance for the BaLa₄Ti₄O₁₅ photocatalyst. The high performance of the BaLa₄Ti₄O₁₅ photocatalyst is due to its high conduction band level, anisotropic crystal structure that enhances charge separation as observed for water splitting, and the suitable combination with a Ni cocatalyst. Kominami and co-workers have reported a high performance for N₂ formation on metal-loaded TiO₂ by NO₃[−] and NO₂[−] reduction in the presence and absence of a hole scavenger [16–18]. These reactions are not accompanied with O₂ evolution, because the hole scavenger and NO₂[−] are oxidized instead of H₂O molecules. This is the significant difference between the TiO₂ and BaLa₄Ti₄O₁₅ systems. Although O₂ evolution is observed for NO₃[−] reduction using Pt/TiO₂ photocatalyst, the main reduction product is NH₃ [3]. So, BaLa₄Ti₄O₁₅ is a unique photocatalyst for NO₃[−] reduction as well as some tantalates [21].

3.2. Effect of pH on photocatalytic NO₃[−] reduction over BaLa₄Ti₄O₁₅

pH of a reactant solution changed from 7 to 12 after 10 h of a photocatalytic reaction time. The change in pH was mainly

Table 2Photocatalytic NO_3^- reduction using an aqueous solution containing H_3BO_3 over $\text{Ni}/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ photocatalyst.

Ni cocatalyst (wt%) ^a	Amounts of products after 10 h/ μ mol					Selectivity ^b (%)	N ₂ yield ^c (%)	e [−] /h ⁺
	Reduction product				Oxidation product			
	H ₂	N ₂	NO ₂ [−]	NH ₄ ⁺				
None	0.5 ^d	4.4 ^d	2600 ^d	0 ^d	1500 ^d	99	0.3	0.9
0.1	500	860	520	12	3200	90	49	0.8
0.3	1000	1100	860	8.4	4000	86	62	0.9
0.5	2400	1500	290	12	5500	76	85	0.9
0.7	1700	1400	300	13	5000	81	80	0.9

Catalyst: 0.5 g, solution: 10 mmol L^{-1} of an aqueous NaNO_3 solution containing 10 mmol L^{-1} of H_3BO_3 (350 mL, initial solution pH 6.9), a 450 W high pressure mercury lamp, an inner irradiation quartz cell,

^a Loading method of cocatalyst: impregnation and H_2 reduction.

^b $(2\text{NO}_2^- + 8\text{NH}_4^+ + 10\text{N}_2)/(2\text{H}_2 + 2\text{NO}_2^- + 8\text{NH}_4^+ + 10\text{N}_2) \times 100$.

^c $(2\text{N}_2)/(\text{an initial amount of } \text{NO}_3^-) \times 100$.

^d After 6 h.

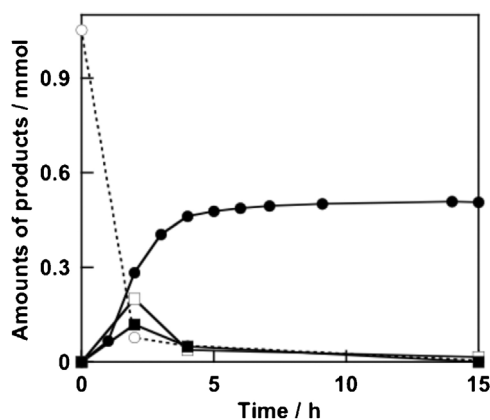


Fig. 1. NO_3^- reduction over $\text{Ni}(0.5 \text{ wt}\%)/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ photocatalyst. Catalyst: 0.5 g, solution: 3 mmol L^{-1} of an aqueous NaNO_3 solution (350 mL) containing H_3BO_3 (0.6 mmol L^{-1}), NO_3^- (\circ), NO_2^- (\square), NH_4^+ (\blacksquare), N_2 (\bullet).

due to formation of NaNO_2 by photochemical and photocatalytic decomposition of NaNO_3 , because NaNO_2 is a basic compound. Elution of a small amount of Ba may also cause the increase in pH. The pH of the reactant solution affects the activity and selectivity for photocatalytic NO_3^- reduction [1]. Therefore, a H_3BO_3 buffer was used to suppress the increase in pH during photocatalytic reaction as shown in Table 2. H_3BO_3 did not affect activity over naked $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$, while it enhanced N_2 formation compared with the case in the absence of H_3BO_3 as shown in Table 1. The effect of H_3BO_3 on the photocatalytic activity was significant at a large loading amount of Ni cocatalyst. N_2 formation was enhanced, while NO_2^- and NH_4^+ were suppressed. This result suggested that the conversion of NO_2^- and/or NH_4^+ to N_2 was enhanced by suppressing an increase in pH. When 0.5% of Ni cocatalyst was loaded, N_2 yield reached 85% for 10 mmol/L of an aqueous NaNO_3 solution. The photocatalytic reduction of NO_3^- (3 mmol/L) on $\text{Ni}(0.5 \text{ wt}\%)/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ in the presence of H_3BO_3 is shown in Fig. 1. NO_3^- was quickly consumed, and NO_2^- and NH_4^+ formed at the beginning stage of the photocatalytic reaction. The NO_2^- and NH_4^+ decreased with N_2 formation. This result suggested that NO_2^- and NH_4^+ were intermediate products for N_2 formation. It should be stressed that more than 80% of NO_3^- was eliminated as N_2 after 4 h of the photocatalytic reaction and almost 100% after 10 h in the present experimental condition.

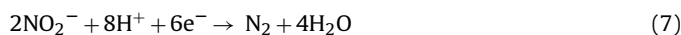
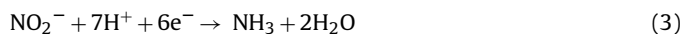
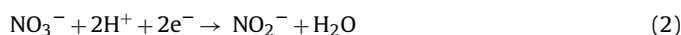
The ratio of the amount of reacted e^- to that of h^+ (Eq. (1)) was almost unity, indicating that the reactions proceeded using water as an electron donor.

$$e^-/h^+ = (2\text{H}_2 + 2\text{NO}_2^- + 8\text{NH}_4^+ + 10\text{N}_2)/4\text{O}_2 \quad (1)$$

Here, NO_2^- and O_2 produced by a photochemical decomposition of NO_3^- [21,30,31] were also supposed by redox reaction in Eq. (1).

3.3. Plausible reaction paths of NO_3^- reduction over $\text{Ni}(0.5 \text{ wt}\%)/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ photocatalyst

Photocatalytic reactions on $\text{Ni}(0.5 \text{ wt}\%)/\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ using aqueous solutions of NaNO_2 and NH_4Cl (3 mmol/L) in addition to NaNO_3 were investigated to see the reaction path of NO_3^- reduction in the presence of a H_3BO_3 buffer as shown in Fig. 2. A N_2 yield higher than 80% was obtained at 4 h of the photocatalytic reaction using an aqueous NaNO_3 solution. Water splitting was enhanced after the consumption of NO_3^- . When the photocatalytic reaction was carried out in an aqueous NaNO_2 solution, the rates of H_2 and N_2 formation decreased. This was mainly due to a filter effect by NO_2^- toward UV. Significant N_2 evolution was not observed when an aqueous NH_4Cl solution was used, indicating that N_2 formation path through oxidation of ammonium ion was negligible in the neutral aqueous solution. The reason why the ratio of e^-/h^+ is deviated from the unity would be due to oxidation of slightly liberated NH_3 to NO_3^- and oxidation of Cl^- . Actually, NO_3^- but not NO_2^- was detected in a liquid phase after the reaction. These results concluded the following reaction paths:



NO_3^- is reduced to form NO_2^- and NH_3 by photogenerated electron in the conduction band of $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ on the Ni cocatalyst as shown in Table 1 (Eqs. (2) and (3)). NO_2^- is also produced by photolysis of NO_3^- (Eq. (4)) [21,30,31]. Because pH increased to 12 in the absence of a H_3BO_3 buffer after the reaction, liberated NH_3 was oxidized to form N_2 as observed for tantalate photocatalysts (Eq. (5)) [21]. Ammonium species mainly exists as NH_4^+ in the reactant solution in the presence of the H_3BO_3 buffer. The NH_4^+ species reacts with NO_2^- on the Ni cocatalyst to form N_2 (Eq. (6)) as reported for thermal catalysis [32]. N_2 could also form by further reduction of NO_2^- (Eq. (7)). O_2 forms by oxidation of water (Eq. (8)) as well as photolysis of NO_3^- (Eq. (4)).

The condition of Ni cocatalyst (0.5 wt%) loaded on $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ before and after the photocatalytic reduction of NO_3^- was observed

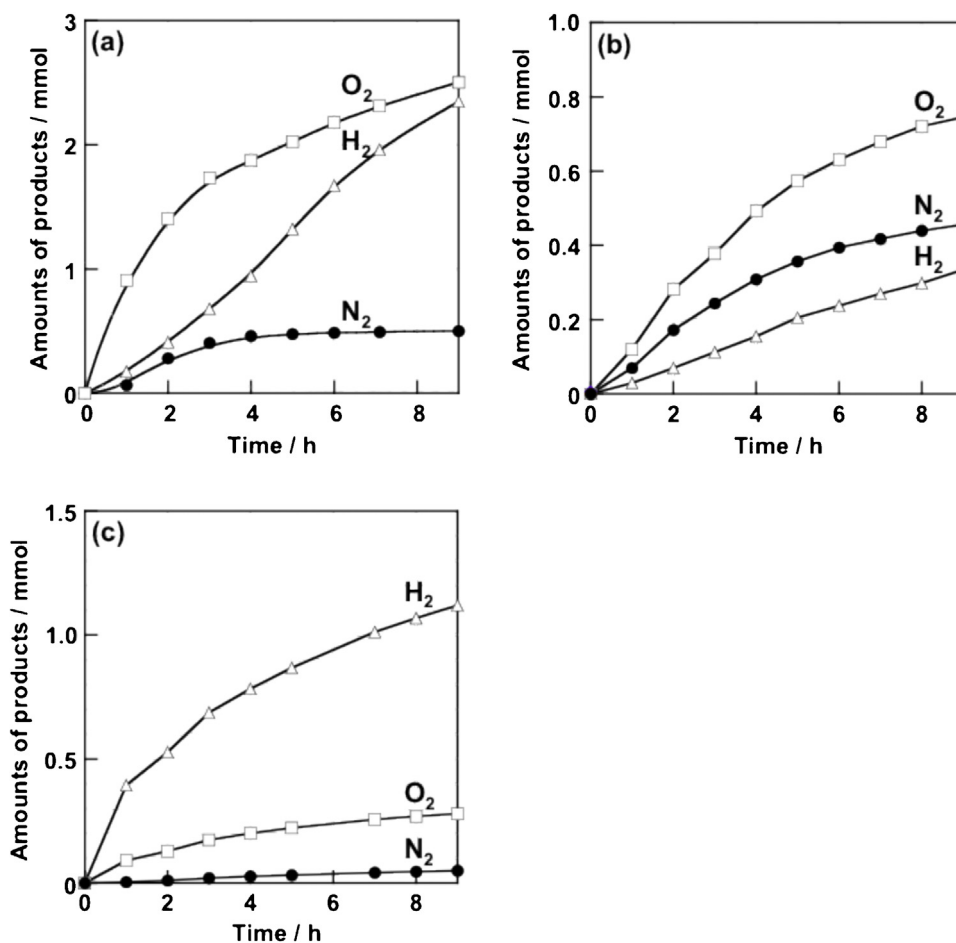


Fig. 2. Gaseous products of photocatalytic reactions over Ni(0.5 wt%)/BaLa₄Ti₄O₁₅ photocatalyst using 3 mmol L⁻¹ of aqueous (a) NaNO₃, (b) NaNO₂, and (c) NH₄Cl solutions (350 mL) containing H₃BO₃ (6 mmol L⁻¹).

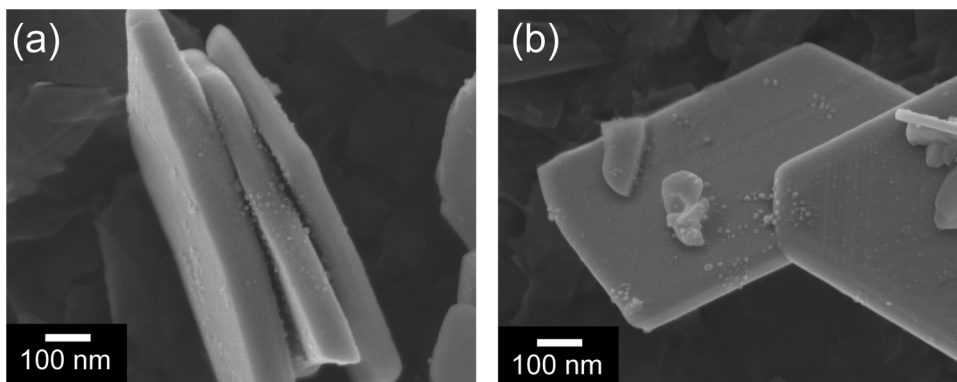


Fig. 3. SEM images of Ni(0.5 wt%)/BaLa₄Ti₄O₁₅ (a) before and (b) after 3 h of photocatalytic reaction.

with SEM as shown in Fig. 3. As-prepared Ni cocatalyst was highly dispersed on the plate-shape surface of BaLa₄Ti₄O₁₅ powder. The condition of the Ni cocatalyst did not change so much after 3 h of the photocatalytic reaction time at which approximately 80% of NO₃⁻ was converted to N₂. This result indicated that the highly dispersed metallic Ni cocatalyst contributed to the high performance for the photocatalytic reduction of NO₃⁻ to N₂.

4. Conclusions

Highly active Ni/BaLa₄Ti₄O₁₅ photocatalyst was developed for NO₃⁻ reduction to harmless N₂ in an aqueous medium. Ni

cocatalyst-loaded BaLa₄Ti₄O₁₅ photocatalyst showed activity for reduction of an aqueous nitrate solution accompanied with O₂ evolution without any sacrificial reagents, indicating that water was consumed as an electron donor. The conversion and selectivity of the photocatalytic reduction of NO₃⁻ strongly depended on the amount of Ni cocatalyst and pH of the reactant solution. The reduction of NO₃⁻ was enhanced compared with that of water, as the amount of Ni cocatalyst increased without pH control. The conversion of NO₃⁻ and the yield of N₂ reached about 90 and 50% after 10 h, respectively. In this case, N₂ was formed by oxidation of NH₃ that was formed by reduction of NO₃⁻. In the presence of a H₃BO₃ buffer, N₂ formed by the reaction of NH₄⁺ with NO₂⁻ on Ni co-catalyst

and also, by further reduction of NO_2^- . Thus, the photocatalytic N_2 formation path in an acidic aqueous solution is different from that in a basic aqueous solution. The high photocatalytic activity for the NO_3^- reduction was caused by highly dispersed Ni cocatalyst loaded on plate shape $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ powder.

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